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THERMOPLASTIC POLYIMIDE NEW-TPI®

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THERMOPLASTIC POLYIMIDE NEW-TPI®

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FOREWORD

This work was sponsored by and performed at the Polymeric Materials Branch (PMB), NASA Langley Research Center (LaRC). Mr. Robert M. Baucom (PMB) was the Technical Monitor for this investigation.

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ABSTRACT

Thermal and rheological properties of a commercial thermoplastic polyimide, NEW-TPI®, were characterized. The as-received material possesses initially a transient crystallite form with a bimodal distribution in peak melting temperatures. After the meltings of the initial crystallite structures, the sample can be recrystallized by various thermal treatments. A bimodal or single modal melting peak distribution is formed for annealing temperatures below or above 360°C, respectively. The recrystallized crystallinities are all transient in nature. The polymers are unable to be recrystallized after being subjected to elevated temperature annealing above 450°C. The recrystallization mechanism was postulated, and a simple kinetics model was found to describe the behavior rather satisfactorily under the conditions of prolonged thermal annealing. Rheological measurements made in the linear viscoelastic range support the evidence observed in the thermal analysis. Furthermore, the measurements sustain the manufacturer's recommended processing window of 400 - 420°C for this material.

INTRODUCTION

Aromatic polyimides have long been recognized to be attractive for applications in the aerospace and electronic industries. The high glass transition temperature, T_g , offered by these polymers is attributed to the stiff molecule backbones which contain aromatic rings. This structure leads to some unique properties such as thermal and thermo-oxidative stabilities at the elevated temperatures; superior chemical resistance and excellent mechanical properties. One of the major problem areas for this class of polymers is its poor processability. For the polymers in fully imidized forms, they are normally insoluble in most organic solvents and mostly infusible at elevated processing temperatures. Consequently in most applications, a polyamide acid solution in a high boiling point or polar solvent must first be prepared, and then converted thermally to polyimide. During the thermal imidization reaction some reaction volatiles are inevitably generated, which demands extra care to ensure a void-free end product. All these characteristics have limited the applications of these polymers.

In order to improve the melt flow properties for this class of materials, various approaches have been investigated in the past. Extensive work has been undertaken in the molecule structure modifications approach [1 - 6]. It was found that introduction of flexible linkages such as $-\text{CH}_2-$, $-\text{O}-$, $-\text{SO}_2-$ into the backbones together with the meta-substituted diamines often lead to enhanced thermoplasticity. Other approaches include the doping of low molecular weight diimide additives [7, 8] and slurry blending of different polymers [9,10]. All these approaches have resulted in degrees of success in enhancing the polymer melt processability, while retaining properties inherent to polyimides.

Mitsui Toatsu Chemical (MTC) Inc. of Japan recently introduced a thermoplastic polyimide with trade name NEW-TPI®. It was reported [11] that this polymer possesses excellent flow properties due to the inclusion of flexible functional linkages between benzene rings and meta substituted diamines in polymer backbone. In this paper we report the thermal and rheological properties of this polymer.

EXPERIMENTAL

The materials investigated in this work were prepared and supplied by MTC. Samples of two different grades were studied as-received without further treatments. The low viscosity grade material is from lot number 6325-3-LV, and is designated hereinafter as MTC-LV. The high viscosity grade material, designated hereinafter as MTC-HV, is from lot number 6326-3-HV. The chemical structure of this polymer is proprietary.

Thermal Properties

A Perkin-Elmer Differential Scanning Calorimeter (DSC) model DSC-7 was used. Samples (3-6 mg) of finely divided polymer were accurately weighed into aluminum sample holders on an analytical balance to 10^{-4} g. A stream of dry nitrogen was continuously flowing over the sample and the reference during measurements. The glass transition temperatures (T_g) and the crystalline melt temperatures (T_m) were determined directly from the thermograms. The heats of fusion were obtained by integrating the areas under the endothermic peaks on the thermograms.

X-Ray Scattering

Wide Angle X-ray Scattering (WAXS) data was obtained on powder specimens of these polyimides. With the X-ray diffractometer operated at 45 kV and 40 mA, using copper radiation with a flat sample holder and a graphite monochromator, the intensity of 1 s counts taken every 0.01° (2θ) was recorded on hard disk for the angular range $5-40^\circ$ (2θ). An external α -quartz standard was used in goniometer alignment.

Rheological Properties

The melt flow properties of these polymers were characterized by linear viscoelasticity. Measurements were performed on a Rheometrics System IV Rotary Rheometer equipped with a parallel plate test fixture. A sample disc of 2.50 cm in diameter was prepared by molding 0.75 g of material at room temperature under a pressure of 5000 psi. The resulting disc was approximately 1.5 mm in thickness. The sample disc was pre-dried in an oven at 100°C for at least 24 hours before use. A dynamic motor was used to drive the top plate to oscillate continuously at a specified amplitude, covering a range of frequency from 0.1 to 100 rad/sec. The bottom plate, which remained stationary during measurement, was attached to a torque transducer which recorded forces. During measurement, the plates and test sample were enclosed in a heated chamber purged with

nitrogen. The chamber and the plates were preheated to the test temperature before loading the sample disc. This was necessary to obtain a precise gap setting.

Strain (oscillating amplitude) levels were selected to assure that the measurements were performed within the material's linear viscoelastic response range and, at the same time, adequate torque values were generated. Repeatability of the measurements performed at each temperature was checked by varying strain values. Such repeatability is also an indication that sample oxidation effect, if any, is negligible. The recorded cyclic torque values were separated into in-phase and out-of-phase components with respect to the oscillatory deformation imposed on the sample, and the corresponding storage (G') and loss (G'') moduli were calculated by the Rheometrics Data Acquisition and Analysis package.

RESULTS AND DISCUSSION

DSC measurements of the as-received materials are shown in Figure 1. Measurements were made at a heating rate of 20°C/min. Double endothermic peaks at 354 and 384°C respectively were observed for both MTC-LV and MTC-HV samples.

The endothermic peaks shown in the DSC thermograms represent the meltings of crystallinity in the polymers. The presence of crystallinity in the as-received samples has been confirmed by X-ray scattering as shown in Figure 2. Identical X-ray diffraction patterns with Bragg angles at 18.0, 22.6, 27.0, 30.1 and 37.2 degrees exists in these two grades of polyimide.

Heat of fusion for the MTC-LV polymer is about $\Delta H = 50\text{-}53$ J/g, while MTC-HV polymer exhibits a lower value of $\Delta H = 46\text{-}49$ J/g. The T_g s were not readily detectable from DSC scans for both as-received materials. It was also found that less than 3% weight loss was recorded for both materials by the thermogravimetric (TGA) measurement during a programmed temperature scan up to 500°C.

Isothermal Recrystallization Behavior

These NEW-TPI® polymers are more readily recrystallizable than the LaRC-TPIs [12, 13]. The recrystallization behavior for samples of MTC-LV subjected to various isothermal treatments at temperatures both above and below the initial crystalline melting peak temperature, $T_0 = 384^\circ\text{C}$, was investigated. In the first set of experiments, the as-received polymer was first heated at a rate of 20°C/min from room temperature (RT) to 420°C, a rapid quenching to a specific isothermal annealing temperature, T_f , below T_0 immediately followed. After the completion of 30 minutes hold times at T_f , a rapid quenching to the ambient temperature was affected. Subsequent thermogram was obtained by rescanning the quenched sample at a rate of 20°C/min to 420°C. The resulting thermograms are shown in Figure 3 for $T_f = 300, 310, 320, 340, 350$ and 360°C .

For $T_f \leq 350^\circ\text{C}$, the recrystallized structures exhibit bimodal crystalline melting peaks. While the higher temperature peak remains constant at 382 - 385°C, the lower temperature peaks are seen to rise in accordance with the increasing of the annealing temperatures. Both peak temperatures and the heat of fusion are tabulated in Table 1. It can be noted that, under such an annealing condition, the heat of fusion is lower than for the initial crystalline form in the as-received sample, and the most favorable recrystallization condition is around $T_f = 340^\circ\text{C}$. The T_g s in the annealed samples are, however, still not readily detectable from the thermograms.

For $T_f \geq 360^\circ\text{C}$, a completely different recrystallization behavior is noted. A typical example at $T_f = 360^\circ\text{C}$ is also included in Figure 3. Here we first see a crystallization exothermic peak at 331°C , followed by a crystalline endotherm with a peak melting temperature at 383°C . The heat of fusion is 36.1 J/g which is lower than the initial value of 52 J/g in the as-received sample. Further more in this case, $T_g = 245^\circ\text{C}$ is readily detectable from the thermogram.

The effect of annealing time at 320°C for samples which have undergone the above described annealing scheme is shown in Figure 4 and Table 2. When compared to the effect of annealing temperature, it is seen that the higher peak temperature remains constant at 384°C , while the lower peak temperatures rise in a slower rate in accordance with the length of annealing time. The heat of fusion also increases with increasing length of annealing time. The degree of crystallinity of the recrystallized structure is again less than the initial crystallinity of the as-received material.

Another set of experiments for the investigation of isothermal recrystallization behavior was conducted as follows: the as-received polymer was first heated at a rate of 20°C/min from RT to a specified T_i above the initial crystalline melting peak temperatures. After the completion of various hold times at temperature T_i , a rapid quenching to ambient temperature followed. Subsequent thermogram was obtained by rescanning the quenched sample at a rate of 20°C/min to 420°C . Isothermal recrystallization behaviors under various annealing conditions are shown in Figures 5-10. Examining the results at $T_i = 420^\circ\text{C}$, Figure 7 for example, the first thermogram obtained at zero minutes annealing time represents the crystalline melting endotherm for the as-received sample. For the samples subjected to various prolonged annealings at the temperature, it is noted that different levels of recrystallization exothermic and crystalline melting endothermic peaks are evident in the thermograms. Unlike other crystalline polymers such as PEEK and LaRC-TPI, the sample was not recrystallized to a higher temperature above T_i during the isothermal annealing, but rather remained amorphous. It can be noted that the recrystallization peak melting temperatures stay around 382°C , which is much lower than the annealing temperature $T_i (= 420^\circ\text{C})$, irrespective of the length of annealing time. The extent of recrystallization reaction is, however, seen to diminish in proportion to the length of the annealing time. In addition, a faster deterioration in the rate of recrystallization is observed for samples subjected to a higher annealing temperature. For example, when a sample was heated up to 550°C and quenched immediately, the recrystallization exotherm was no longer observable during the next scan. The heats of fusion measured for the MTC-LV samples subjected to isothermal annealing as described above are tabulated in Table 3. Values of T_g remain at a constant value around 248°C , irrespective of the annealing conditions.

Based on Table 3, an annealing time-temperature processing window for this polymer can be established as shown in Figure 11. This diagram provides the processing window in which the occurrence of the recrystallization phenomenon in the MTC-LV polymer is not suppressed.

The observed recrystallization behavior of this polymer differs from that of a Liquid Crystalline Polymer (LCP), such as VECTRA A900 (Celanese Corp.) [14, 15], in two basic ways: (i) a crystalline solid with higher ordered structure was unable to be formed during isothermal annealing of the polymer melt, and (ii) the exhibition of thermo-irreversible recrystallization behavior, which was clearly shown by the recrystallization of isothermal annealing at elevated temperatures, was evident.

Dynamic Recrystallization Behavior

The dynamic recrystallization behavior was investigated by conducting consecutive thermal treatments in the DSC where the sample was heated from RT, at a rate of 20°C/min to a specific temperature, T_d , higher than the initial crystalline melting peak temperatures and followed by a rapid quenching. Thermograms of five consecutive DSC scans to $T_d = 415^\circ\text{C}$ for the MTC-LV material are shown in Figure 12. The thermogram of the first scan represents the initial crystalline melting endotherm of the as-received polymer. At the end of the first scan, a rapid quenching followed. In each of the subsequent scans, a recrystallization exothermic peak at 330°C, followed immediately by a crystalline melting endothermic peak, is clearly visible. The recrystallization peak melting temperature remains the same at about 384°C which is close to the initial crystalline melting peak temperature, but much lower than the highest temperature ($T_d = 415^\circ\text{C}$) scanned. This indicates that the sample was amorphous at the end of each heat-up scan by the DSC. It is noted that, under such a thermal treatment, the heat of fusion is reduced from 51 J/g in the as-received sample to a constant value of 32 J/g, irrespective of number of scans. The glass transition temperature, T_g , became visible after the first scan as well. T_g remains constant at around 248°C.

Similar experiments performed at $T_d = 450^\circ\text{C}$ for the MTC-LV polymer are shown in Figure 13. Similar behavior can be noted from these thermograms. Although values of T_g remain the same at 248°C, the heat of fusion for the recrystallized crystalline form is, however, reduced to a constant value of about 29 J/g.

Dynamic recrystallization behavior for the MTC-HV polymer was also investigated at two temperatures, $T_d = 450$ and 500°C , as shown in Figures 14 and 15. In each case, a constant value of $T_g = 248^\circ\text{C}$ is attainable after the first scan. Similar recrystallization behavior to those exhibited by the MTC-LV samples is observed. The heat of fusion is,

however, further reduced from 48 J/g in the as-received sample to about 10 J/g under the thermal treatment at $T_d = 450^\circ\text{C}$. These results indicate that the MTC-HV polymer is less readily recrystallizable than the MTC-LV polymer. It shows that the recrystallization behavior of both grades of polymer depends on the thermal histories of the samples, and the elevated temperatures are less favorable conditions for recrystallization to occur.

Recrystallization Kinetics

It has been shown that the recrystallization behavior of this polyimide is not thermoreversible. After prolonged annealing at elevated temperatures ($> 400^\circ\text{C}$), the recrystallization is suppressed. Higher annealing temperature leads to a smaller degree of recrystallization. Evidence from the rheological measurements, as discussed in the next section, indicates that certain polymerization reactions occur at these elevated temperatures.

It is expected that the recrystallization occurs in the nucleation and the growth steps. The nucleation rate is much lower than the growth rate. For the polymer studied here, the C-C backbones in the molecules are rather stiff. A likely nucleation path is the intermolecular oligomer nucleation type [16]. A certain oligomer concentration must first be formed before nucleation can occur, and crystallization during polymerization can commence. Therefore, when the sample was subjected to prolonged annealing at elevated temperatures, the polymerization reactions led to a suppression in the degree of recrystallization due to an insufficient concentration of nuclei.

The observed diminishing recrystallization capabilities for samples subjected to prolonged isothermal annealing at the elevated temperatures could be modeled with a simple kinetics by defining that at a given T_i ,

$$\frac{Q(t)}{Q(0)} = 1 - x \quad (1)$$

where $Q(t)$ are the values tabulated in Table 3; $Q(0)$ is the heat of fusion of a sample subjected to zero time ($t = 0$) annealing; and $(1 - x)$ is the fraction of the remaining species (short chain molecule segments) in the sample which are capable of forming the nucleation sites at time t . Then

$$\frac{dx}{dt} = k(1 - x)^n \quad (2)$$

where

$$k = k_0 \exp [- E_a/RT] \quad (3)$$

with k [sec^{-1}], the recrystallization reaction rate constant; n , the reaction order; E_a [cal/mole], the activation energy of recrystallization; and $R = 1.986$ [cal/mole/°K], the universal gas constant. Eq. (2) can be integrated to become

$$y^{-\alpha} = \alpha k t \quad (4)$$

with $\alpha = n-1$ and $y = 1 - x$.

Comparisons between Eq. (4) and the experimental measurements of Table 3 are shown in Figure 16. Except in the regime of short annealing times of each annealing temperature, a favorable comparison is noted. The kinetic parameters are tabulated in Table 4. It is seen that the reaction order remains at $n = 4.0$, independent of the annealing temperature T_i . The rate constant k , however, increases with increasing T_i , and can be satisfactorily described by Eq. (3), as shown in Figure 17, with a linear correlation coefficient better than 0.989. The activation energy of recrystallization is found to be $E_a = 56$ cal/mole.

Linear Viscoelastic Behavior

The linear viscoelastic properties, $G'(t)$ and $G''(t)$, measured at angular frequency of 10 rad/sec under three isothermal conditions are shown in Figure 18. At each temperature both moduli are seen to increase monotonically during the duration of the experiment. As shown before, the sample is in the amorphous state when annealed at the elevated temperatures above 400°C. The observed increases in moduli could, therefore, be attributed to the polymerization reactions through chain extensions or ring closures. In fact, minor reactions that occurred within the sample during the rheological measurement were noticeable. Approximately 2% weight loss was measured by TGA for sample heated up to 450°C which supports the argument for chain extension or ring closure occurring at the elevated temperatures.

In the early stages of the measurements shown in Figure 18, it is noted that the loss modulus, G'' , has a higher value than the storage modulus, G' , for both 400 and 410°C measurements. Such a viscoelastic liquid-like behavior does not exist for temperatures above 430°C, and persists for only a relatively short period of time (40 and 20 minutes, respectively, for the 400 and 410°C conditions). In this regime, the melt viscosities are in the range of $10^3 - 10^4$ poises. This compares favorably to the reported values by the

manufacturer [17] and explains the manufacturer recommended processing window of 400 - 420°C for this material for the Compression and Injection Moulding operations.

CONCLUSIONS

Thermal and rheological properties of two grades of a thermoplastic polyimide NEW-TPI® are characterized. The as-received materials possess a transient crystallite form which exhibits a bimodal distribution with melting peak temperatures located at 354 and 384°C. After the melting of the initial crystallites in the as-received sample, the material can be readily recrystallized to a bimodal crystalline structure when annealed at temperatures below 360°C. The lower peak of such a recrystallized material rises to a higher temperature with increased annealing temperatures and the lengths of annealing time, while the higher peak remains at a constant temperature around 385°C. The degree of crystallinity in the recrystallized structure is, however, less than that possessed initially in the as-received sample.

For the annealing temperature above 360°C, a completely different recrystallization behavior is observed. Samples at these annealing temperatures are purely amorphous. After the sample is quenched to RT from the annealing temperature and subsequently heated in the DSC, a crystallization exotherm is first seen, and is followed immediately by a crystalline melting endotherm. The sizes of the recrystallization exotherm and the crystalline melting endotherm decrease with an increase in the annealing temperature and time. However, the recrystallization peak melting temperature stays constantly around 382°C. Such behavior leads to a postulation that the nucleation path in the recrystallization reaction is the intermolecular oligomer nucleation type. When the sample was subjected to prolonged annealing at elevated temperatures, the polymerization reactions lead to a suppression in the degree of recrystallization due to insufficient concentration of nuclei. A simple kinetics model is proposed to illustrate such a behavior. Such thermo-irreversible behavior also distinguished this polymer from the class of Liquid Crystal Polymers (LCPs).

Rheological measurements made in the linear viscoelastic region support the evidence observed in the thermal analysis. Furthermore, the measurements sustain the manufacturer's recommended processing window of 400 - 420°C for this material.

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Table 1. Recrystallization behavior for samples annealed 30 minutes at given temperatures after meltings of initial crystallinities at 420°C

T_f (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH (J/g)
300	316.7	385.1	32.5
310	326.1	385.2	35.6
320	333.9	383.7	35.3
330	340.0	382.7	38.4
340	352.7	381.5	40.8
350	360.5	385.0	39.1
360	---	382.9	36.1
370	---	382.5	32.7

Table 2. Recrystallization behavior for samples annealed at 320°C after meltings of initial crystallinities at 420°C

Annealing time t(min)	T _{m1} (°C)	T _{m2} (°C)	ΔH (J/g)
15	332	384	36.7
30	334	384	35.3
60	336	384	37.1
120	338	384	40.5

Table 3. Heat of Fusion for MTC-LV Polymer Subjected to Isothermal Annealing of Various Lengths of Time Under Each Temperature

$T_i(^{\circ}\text{C})$ t(mins)	400	410	420	430	440	450
0	49.12	50.04	50.92	49.03	50.72	51.94
5	--	--	--	--	35.12	--
10	--	--	--	--	25.06	--
15	--	--	--	30.29	16.64	3.39
20	--	--	--	--	11.05	--
25	--	49.81	--	--	6.61	--
30	--	--	31.40	13.44	3.38	--
45	--	--	--	0.68	--	--
50	--	--	18.46	--	--	--
55	--	41.59	--	--	--	--
60	--	--	--	--	--	--
65	--	--	8.83	--	--	--
75	--	--	5.38	--	--	--
85	--	23.75	--	--	--	--
115	--	10.54	--	--	--	--
120	--	--	--	--	--	--
145	--	4.54	--	--	--	--
150	--	--	--	--	--	--
175	--	2.02	--	--	--	--
180	24.43	--	--	--	--	--
270	12.96	--	--	--	--	--
390	4.12	--	--	--	--	--

Table 4. Kinetics Parameters in Eq. (1) for MTC-LV Polymer Annealed Under Various Isothermal Conditions

$T_i(^{\circ}\text{C})$	k	n
410	0.005	4.0
420	0.0095	4.0
430	0.02	4.0
440	0.027	4.0

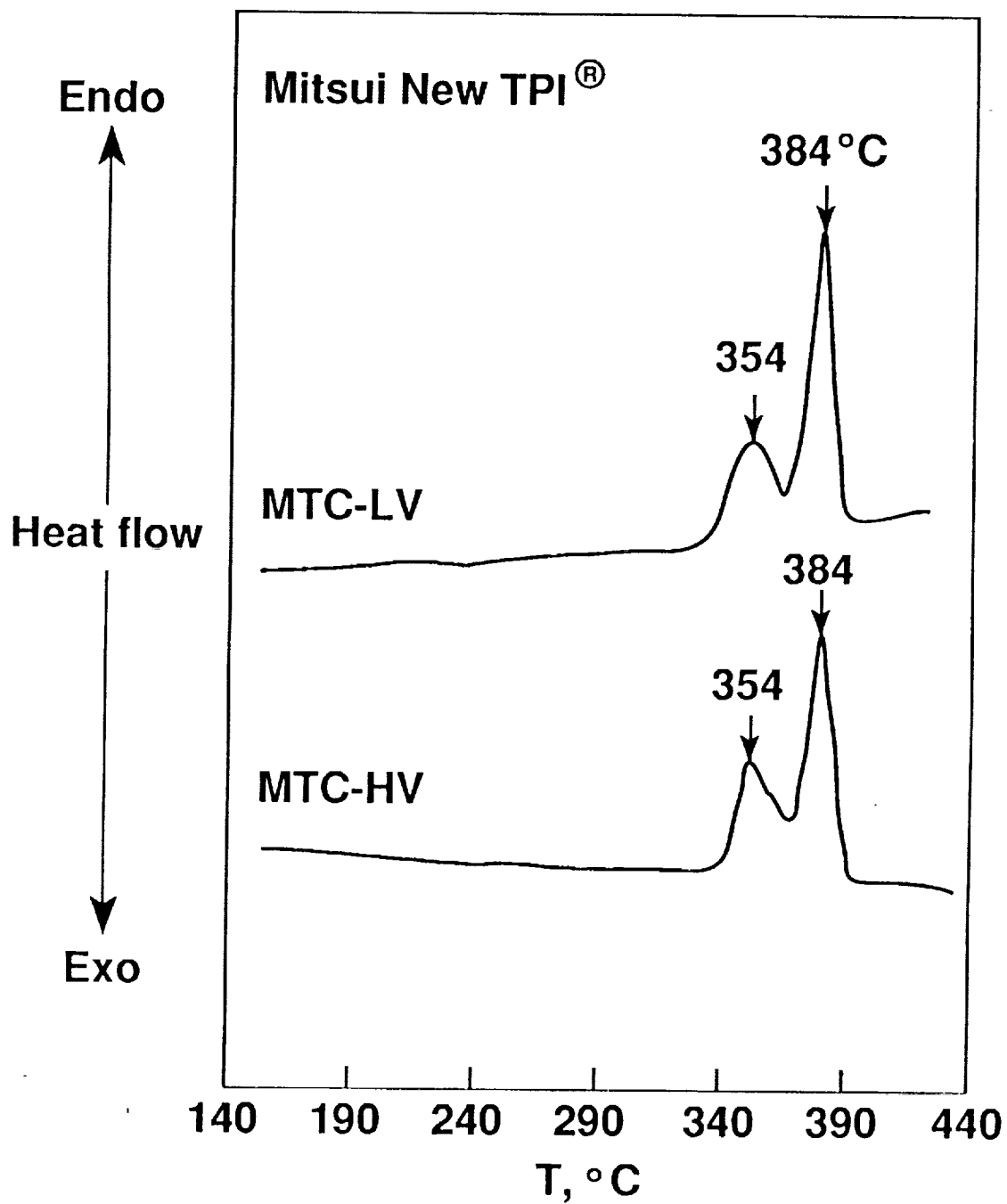


Figure 1. DSC thermograms of the two grades of as-received Mitsui NEW-TPI[®] polymers.

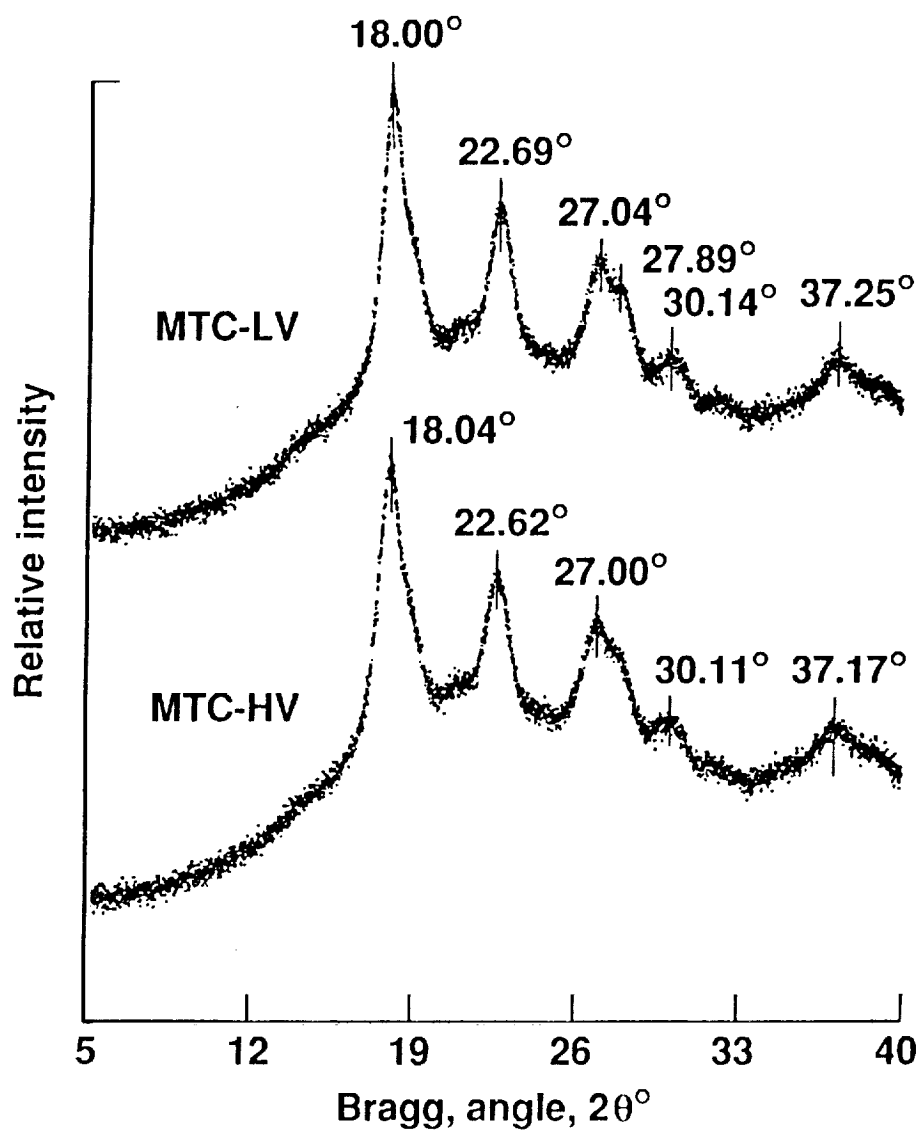


Figure 2. WAXS diffractograms for the two grades of as-received Mitsui NEW-TPI® polymers.

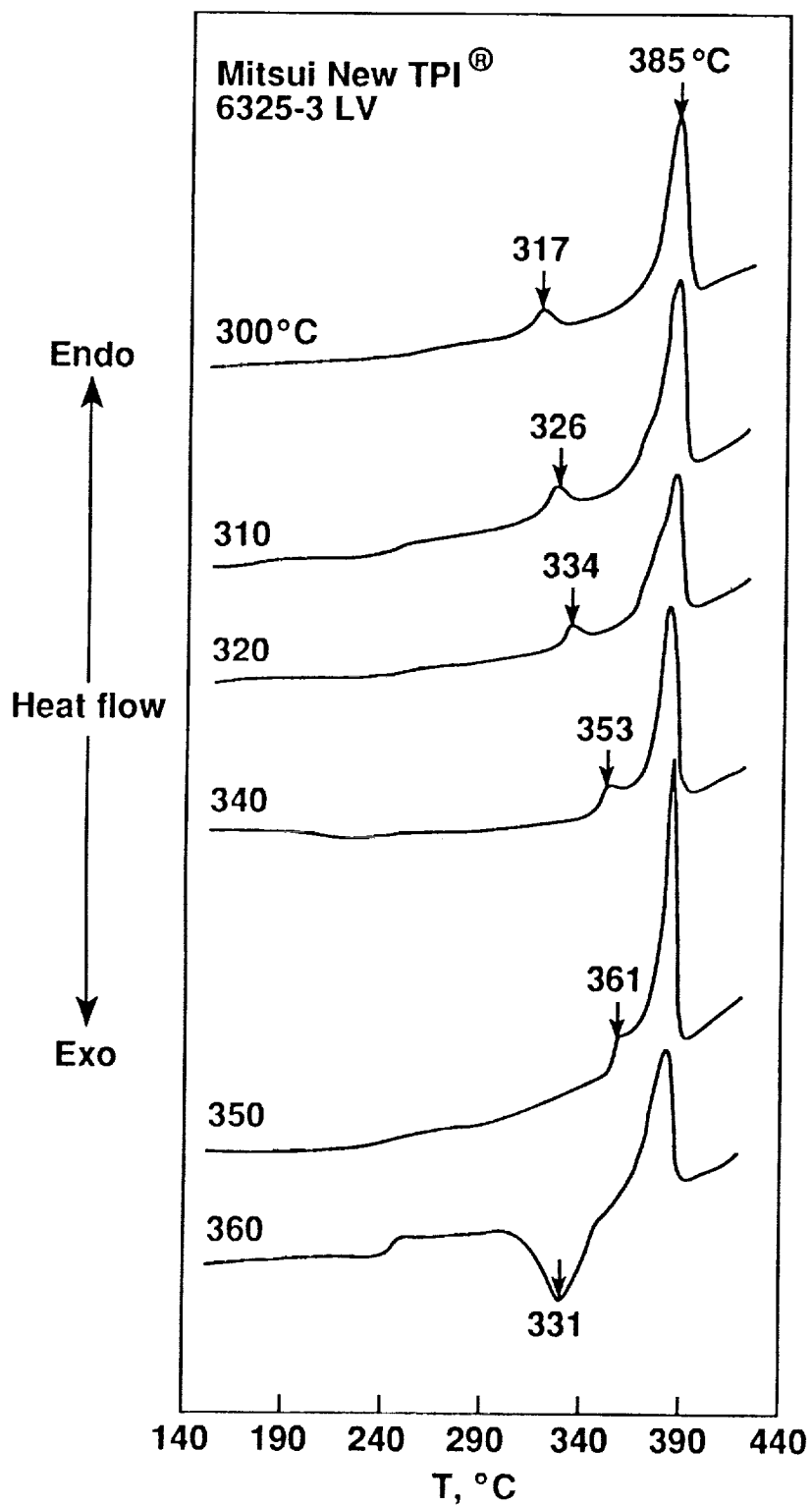


Figure 3. DSC thermograms of the MTC-LV samples annealed for 30 minutes at the temperatures indicated. The samples were first subjected to a thermal history of heat up scan from RT to 420°C.

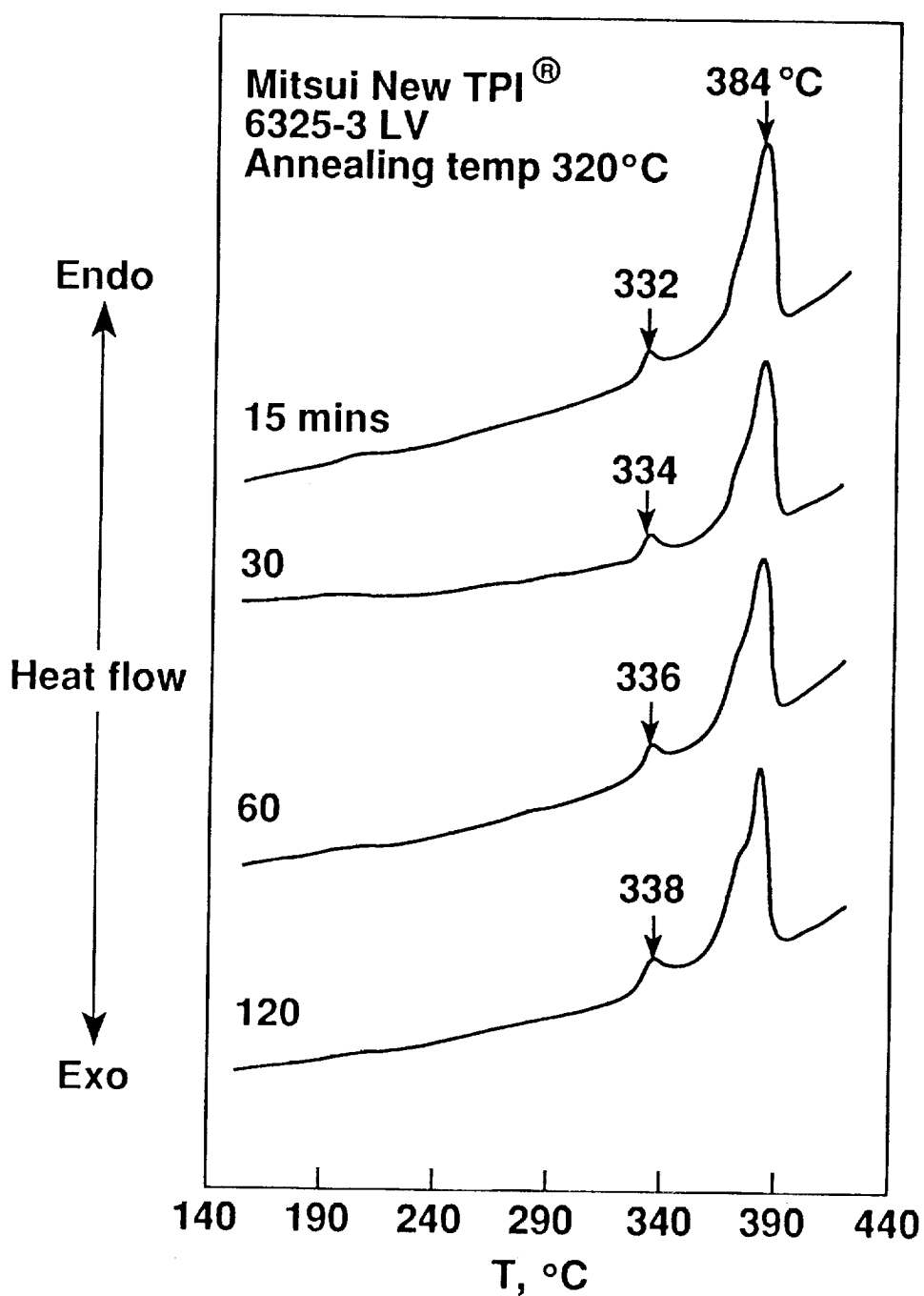


Figure 4. DSC thermograms of the MTC-LV samples annealed at 320°C for various lengths of time indicated. The samples were first subjected to a thermal history of heat up scan from RT to 420°C.

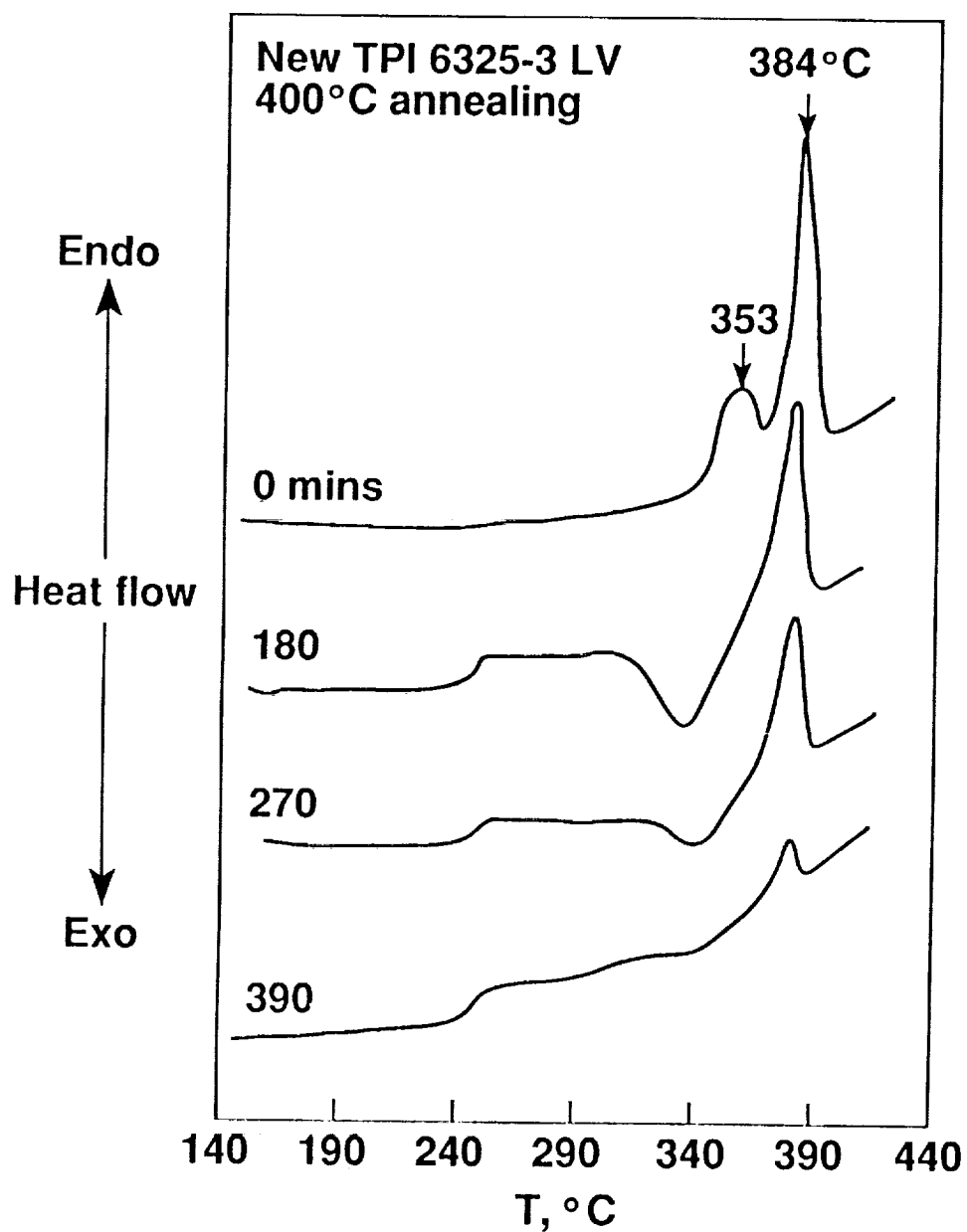


Figure 5. DSC thermograms of the MTC-LV samples annealed at 400°C for various lengths of time indicated. The samples were first subjected to a thermal history of heat up scan from RT to 420°C.

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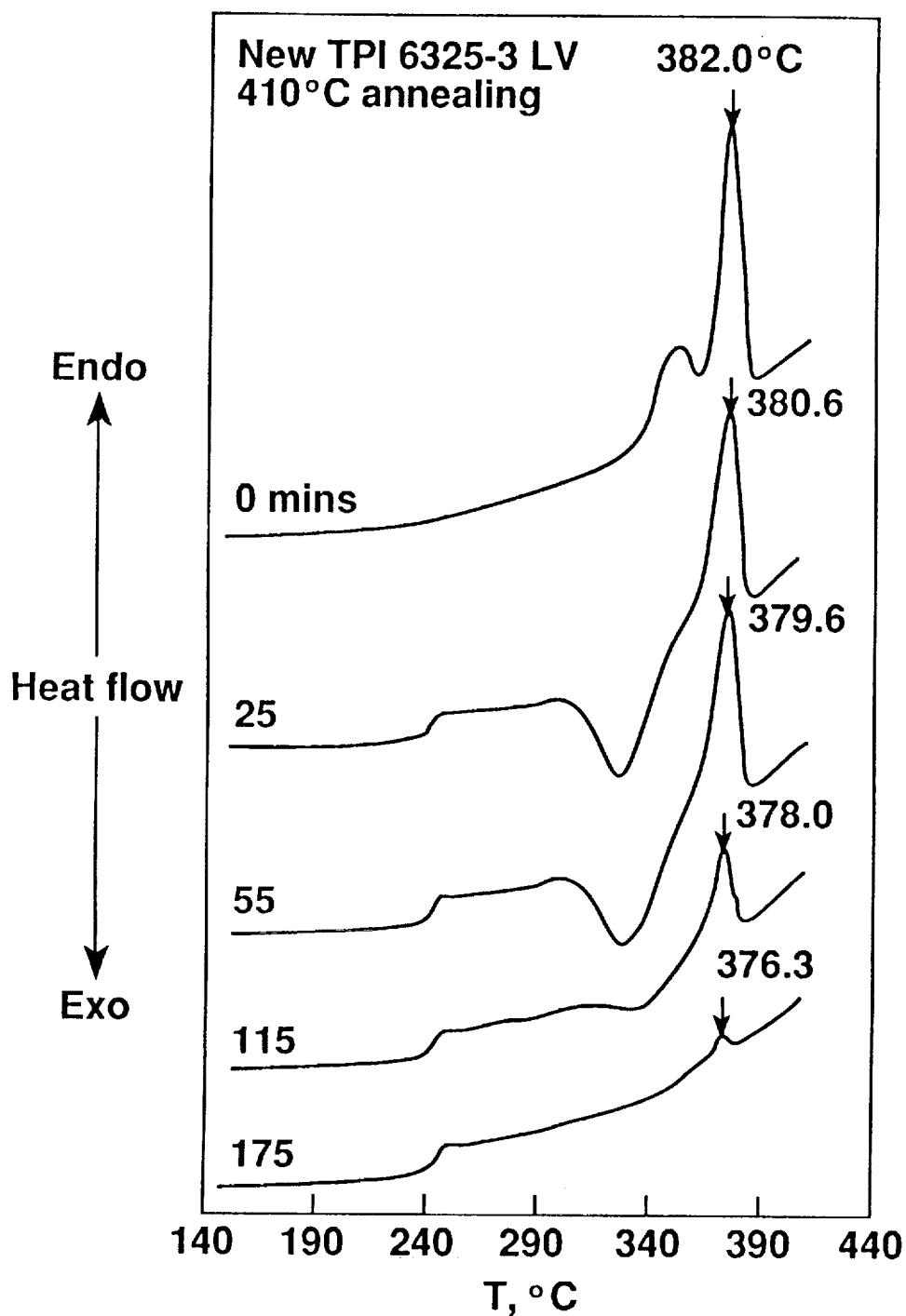


Figure 6 DSC thermograms of the MTC-LV samples annealed at 410°C for various lengths of time indicated. The samples were first subjected to a thermal history of heat up scan from RT to 420°C.

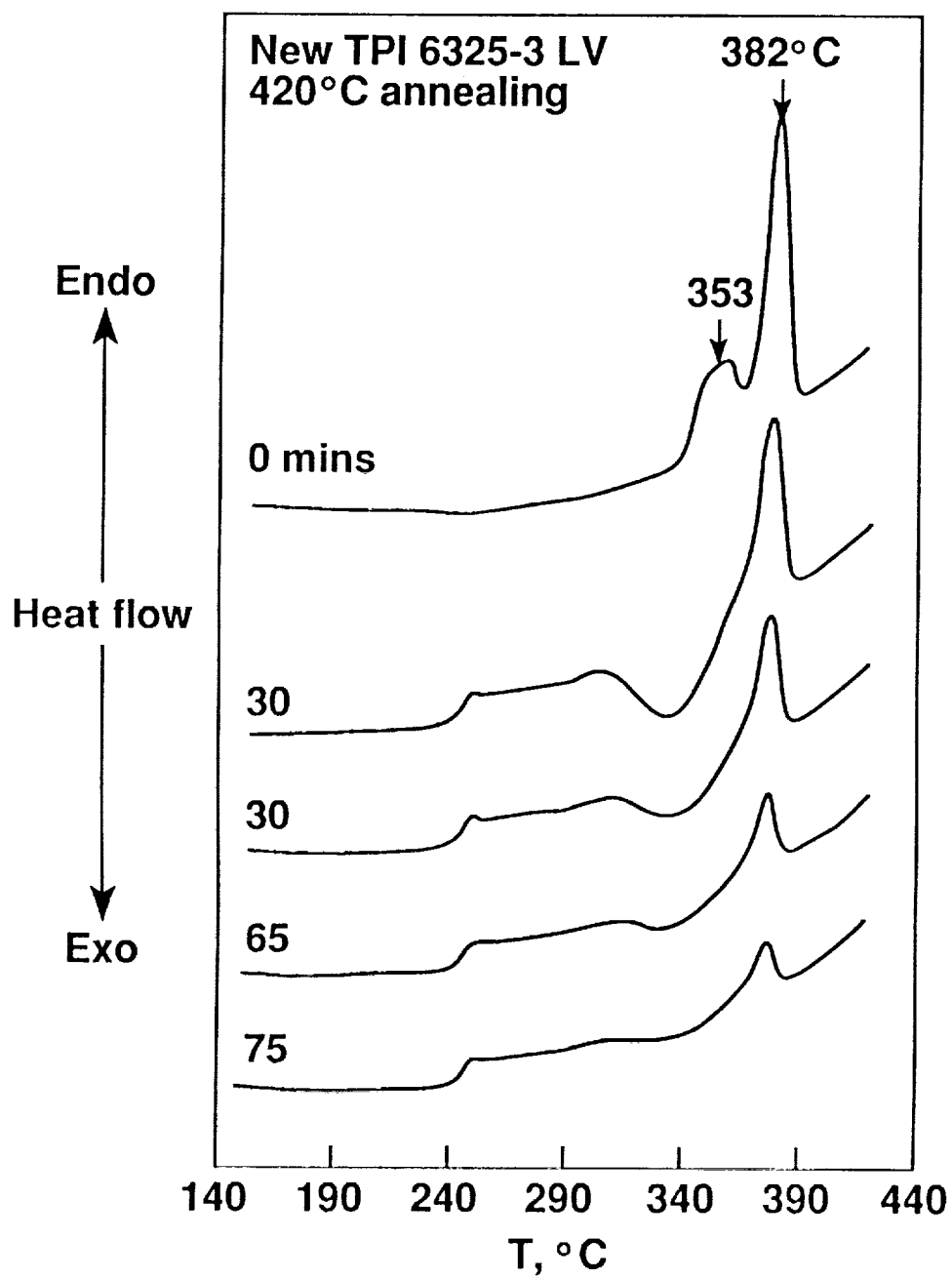


Figure 7. DSC thermograms of the MTC-LV samples annealed at 420°C for various lengths of time indicated.

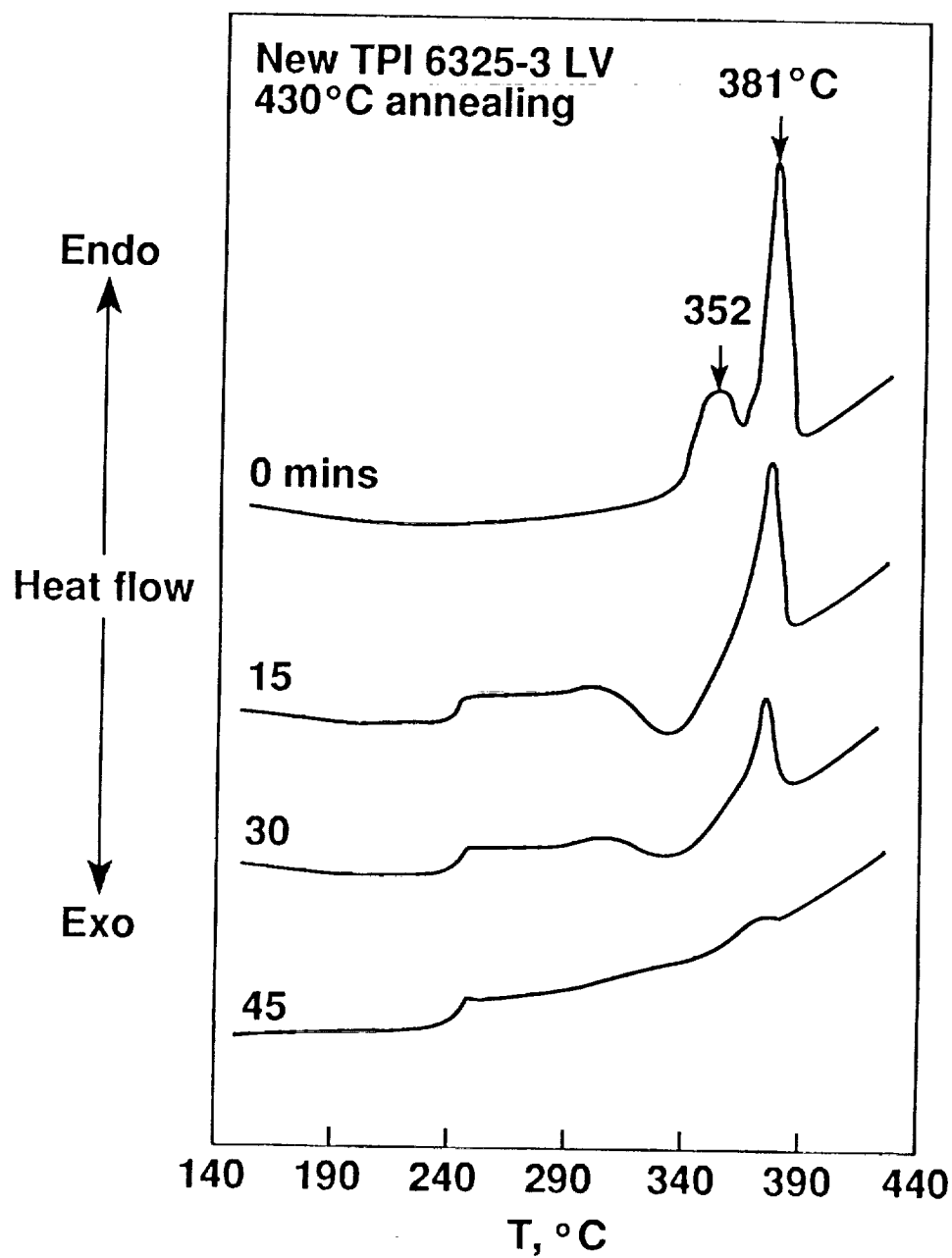


Figure 8. DSC thermograms of the MTC-LV samples annealed at 430°C for various lengths of time indicated.

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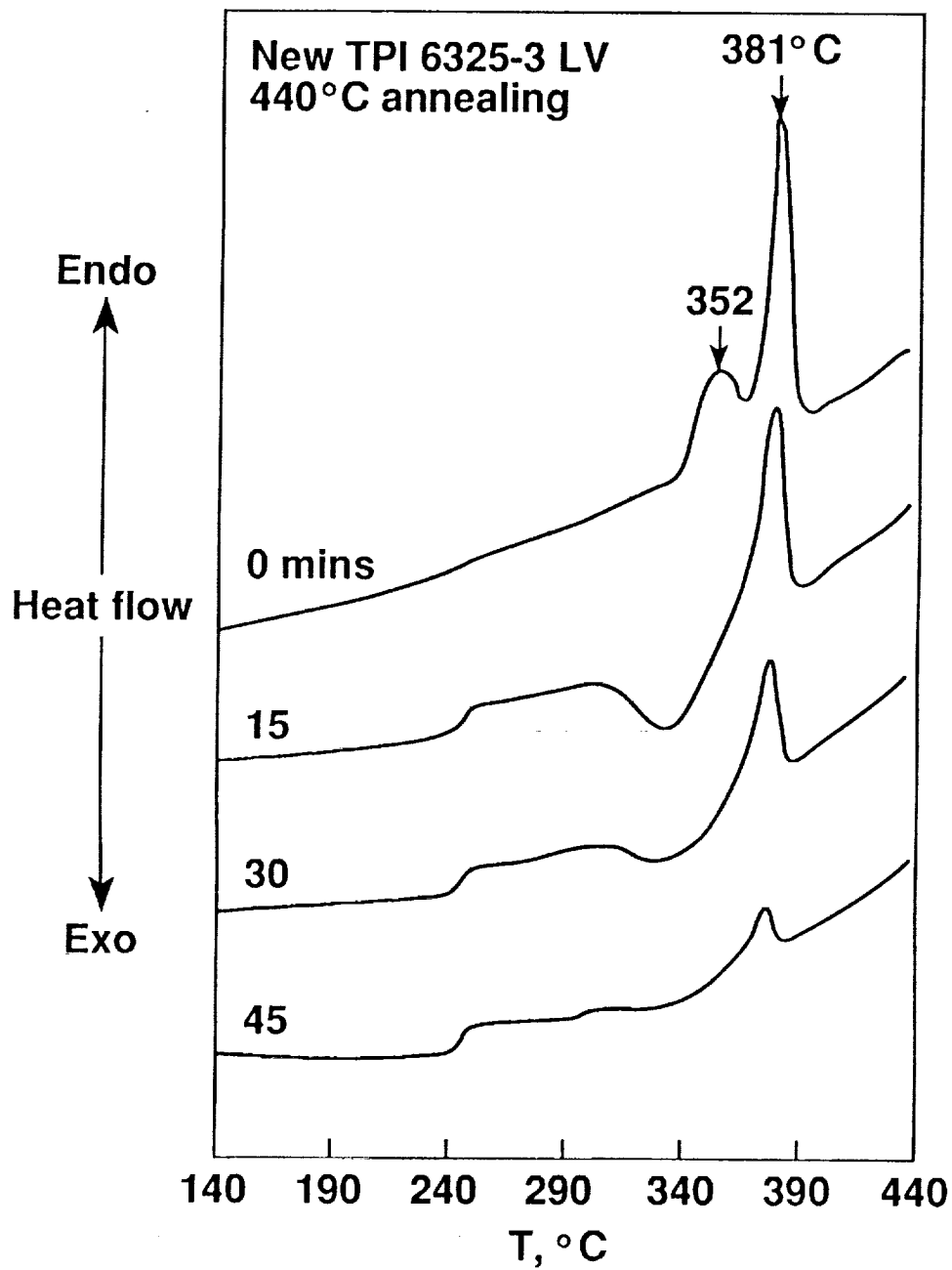


Figure 9. DSC thermograms of the MTC-LV samples annealed at 440°C for various lengths of time indicated.

12/7/95

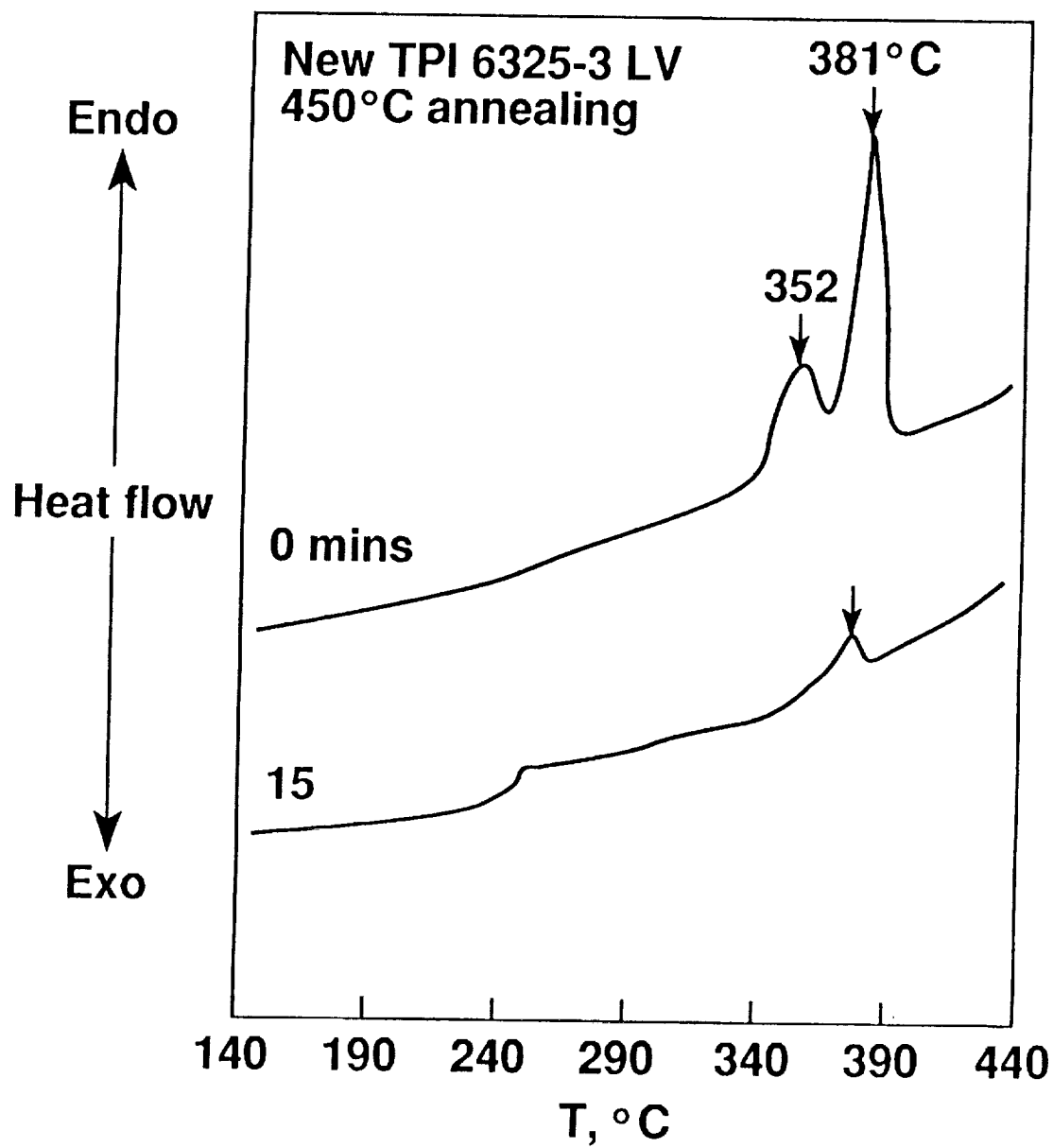


Figure 10. DSC thermograms of the MTC-LV samples annealed at 450°C for various lengths of time indicated.

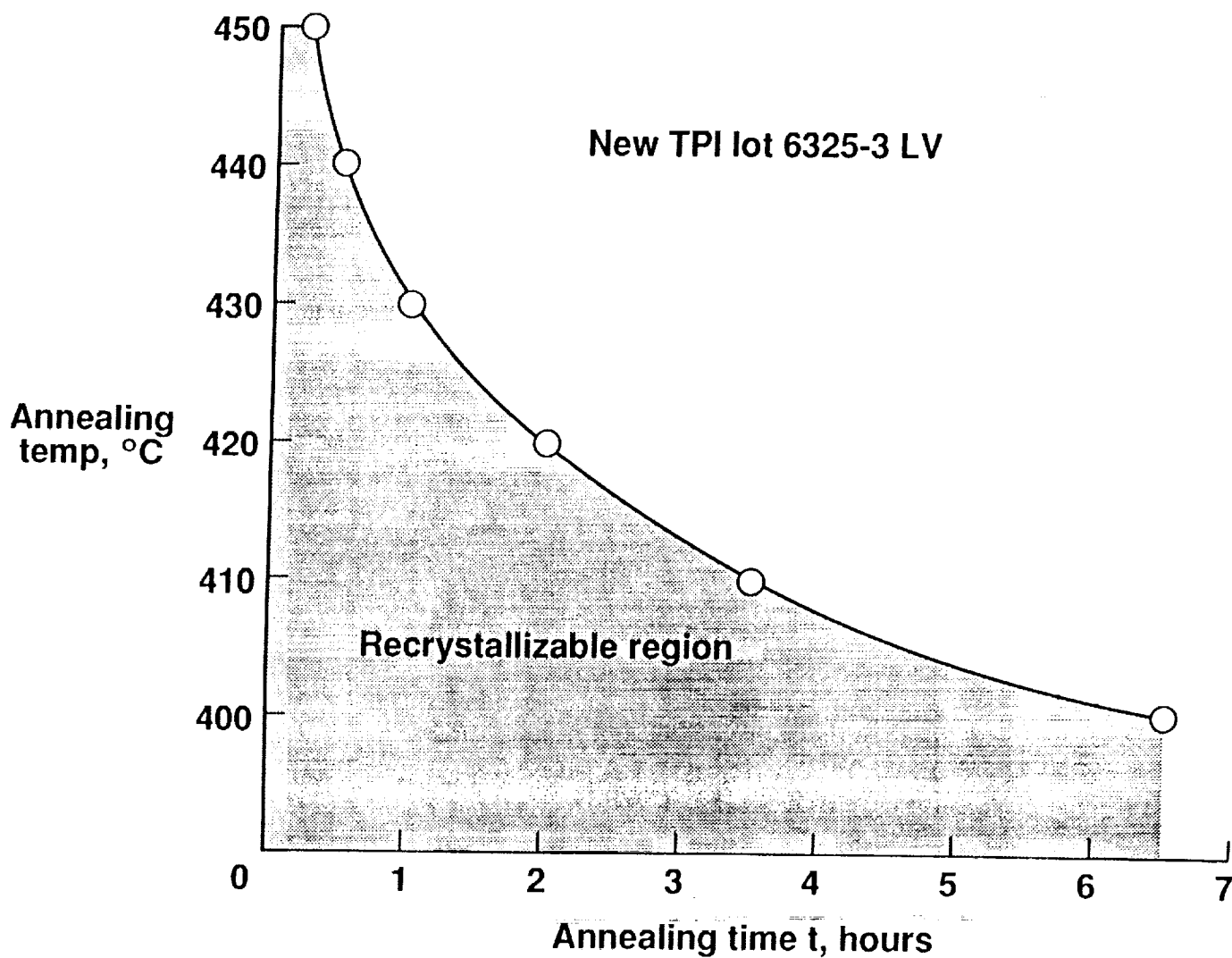


Figure 11. Temperature-time processing window in which the recrystallization capabilities of the MTC-LV samples are not completely suppressed.

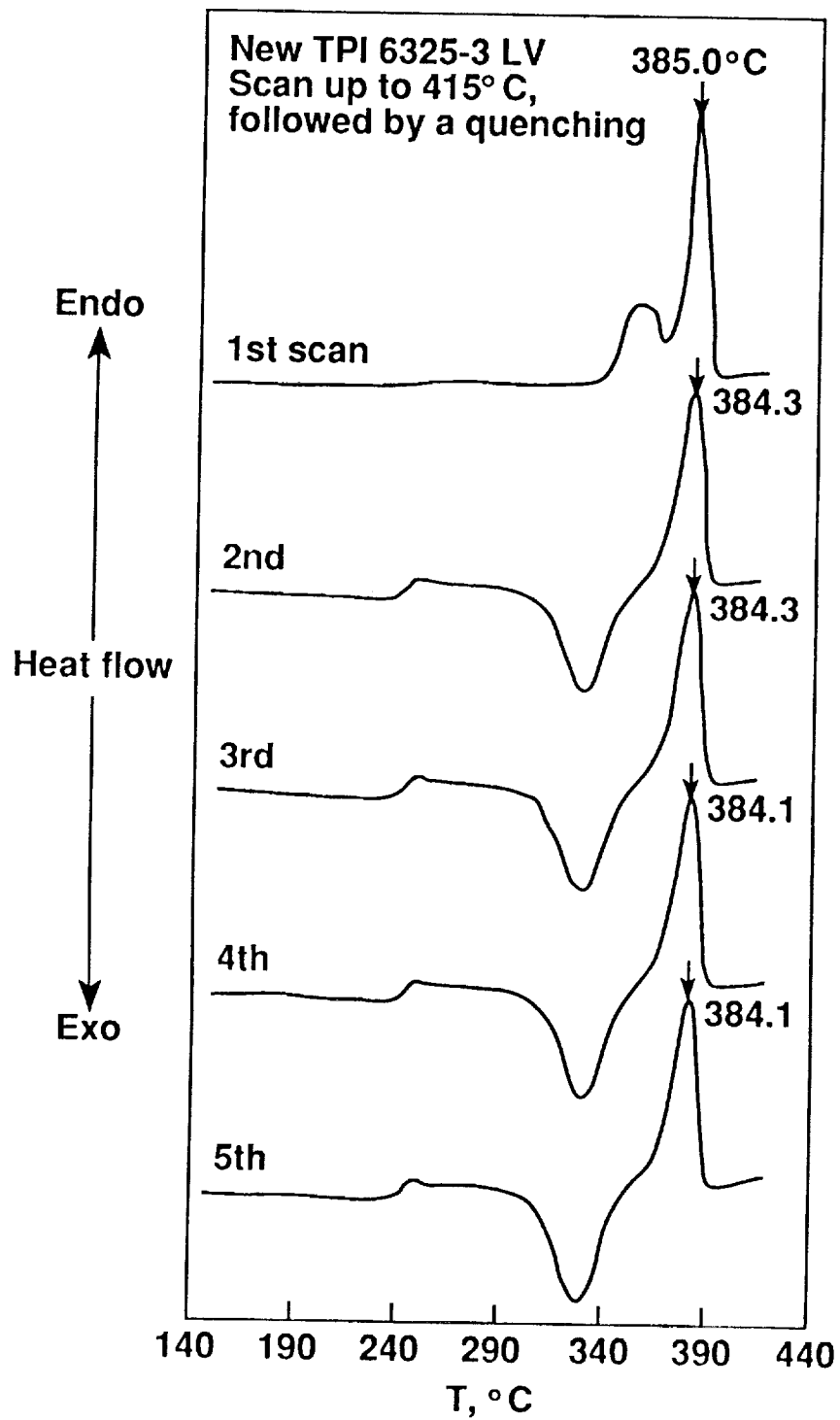


Figure 12. DSC thermograms of the MTC-LV samples subjected to consecutive temperature scans from RT to 415°C.

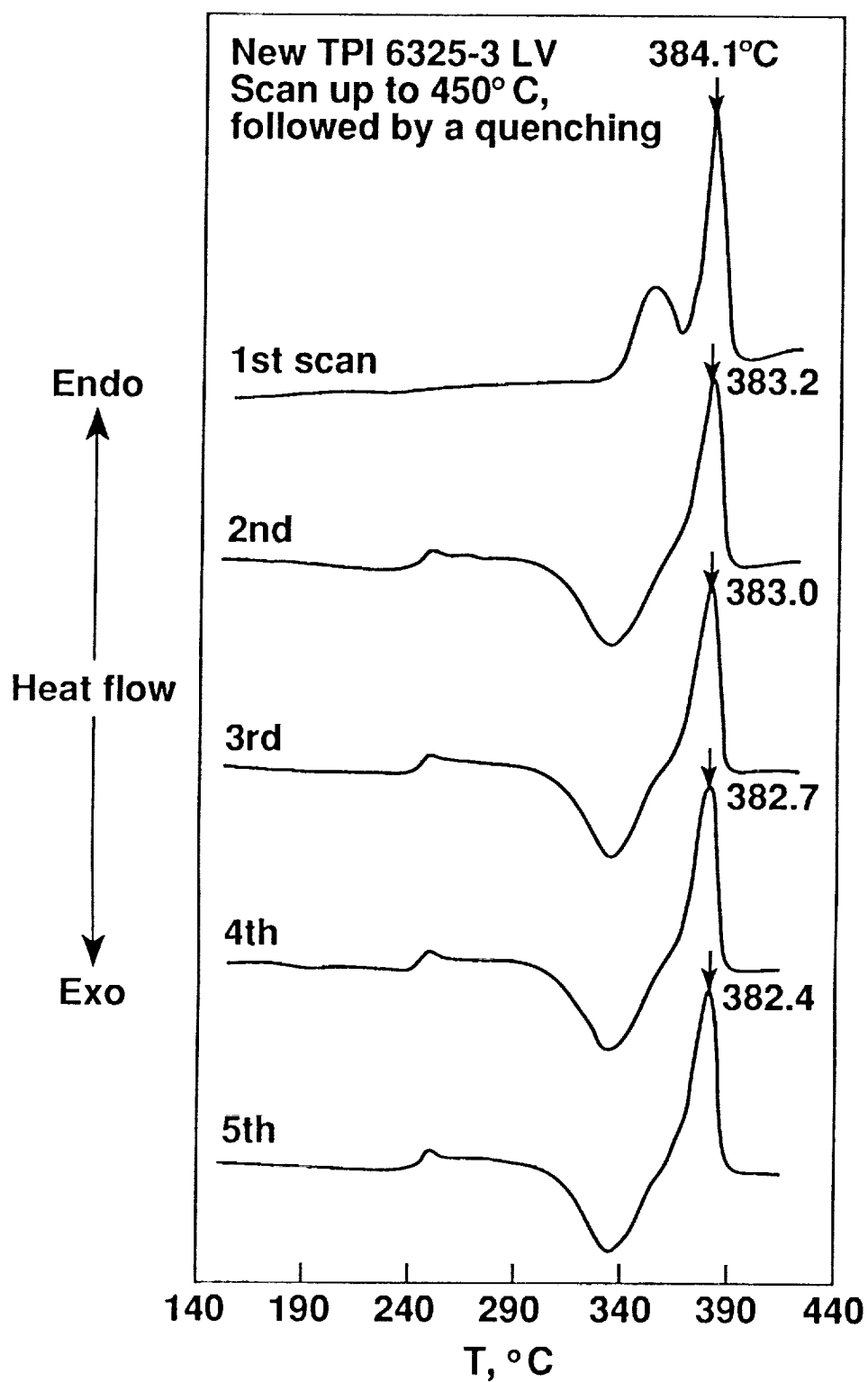


Figure 13. DSC thermograms of the MTC-LV samples subjected to consecutive temperature scans from RT to 450°C.

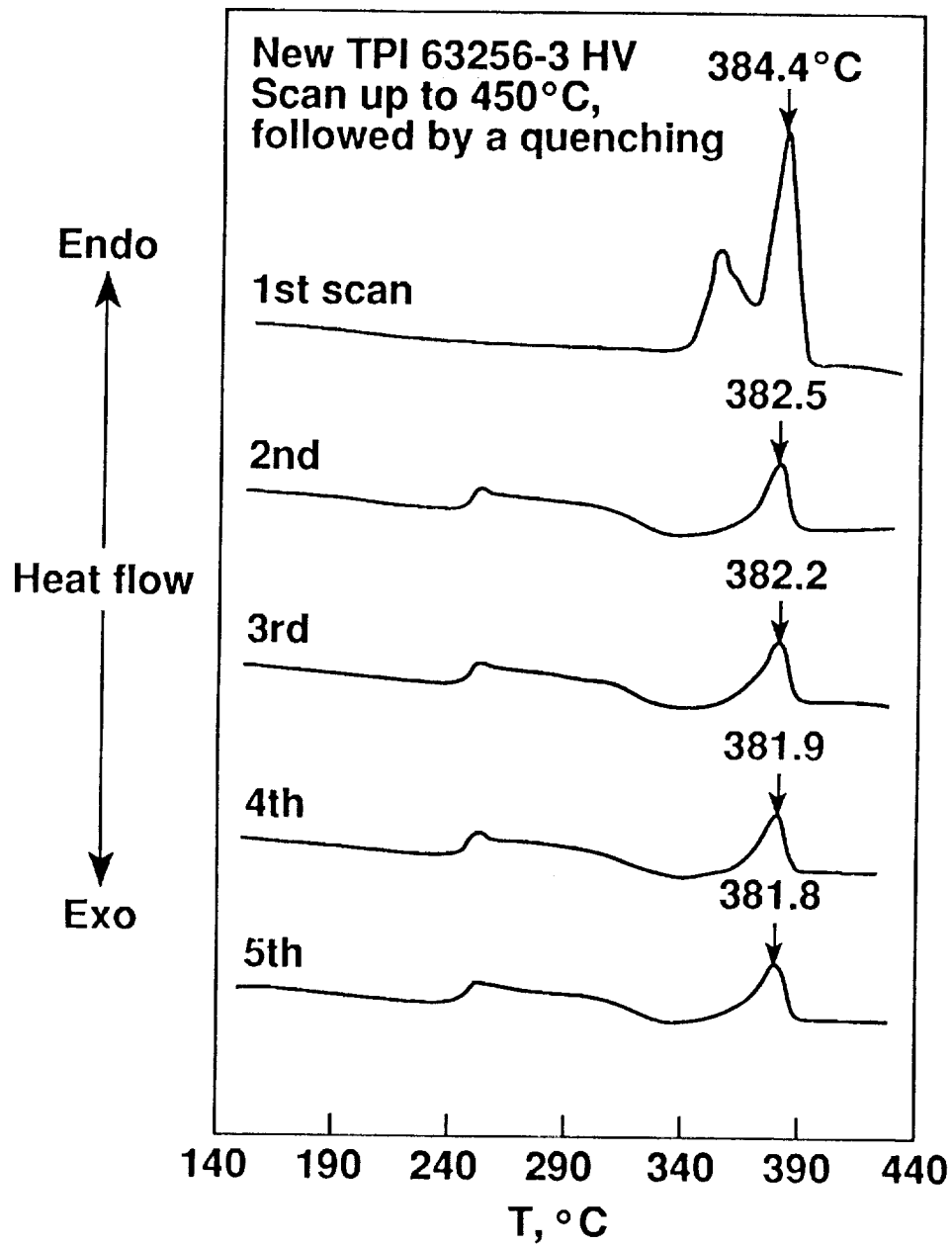


Figure 14. DSC thermograms of the MTC-HV samples subjected to consecutive temperature scans from RT to 450°C.

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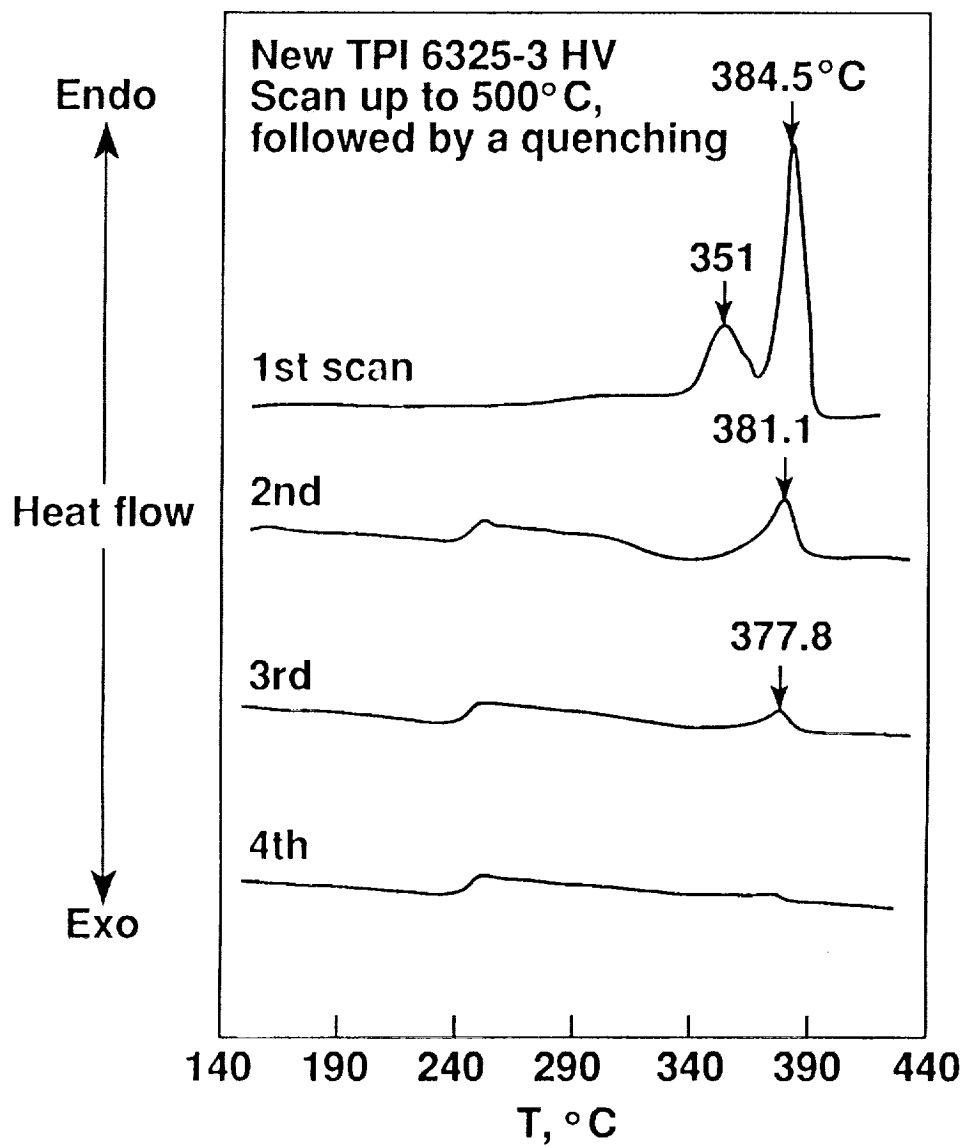


Figure 15. DSC thermograms of the MTC-HV samples subjected to consecutive temperature scans from RT to 500°C.

12/7/98

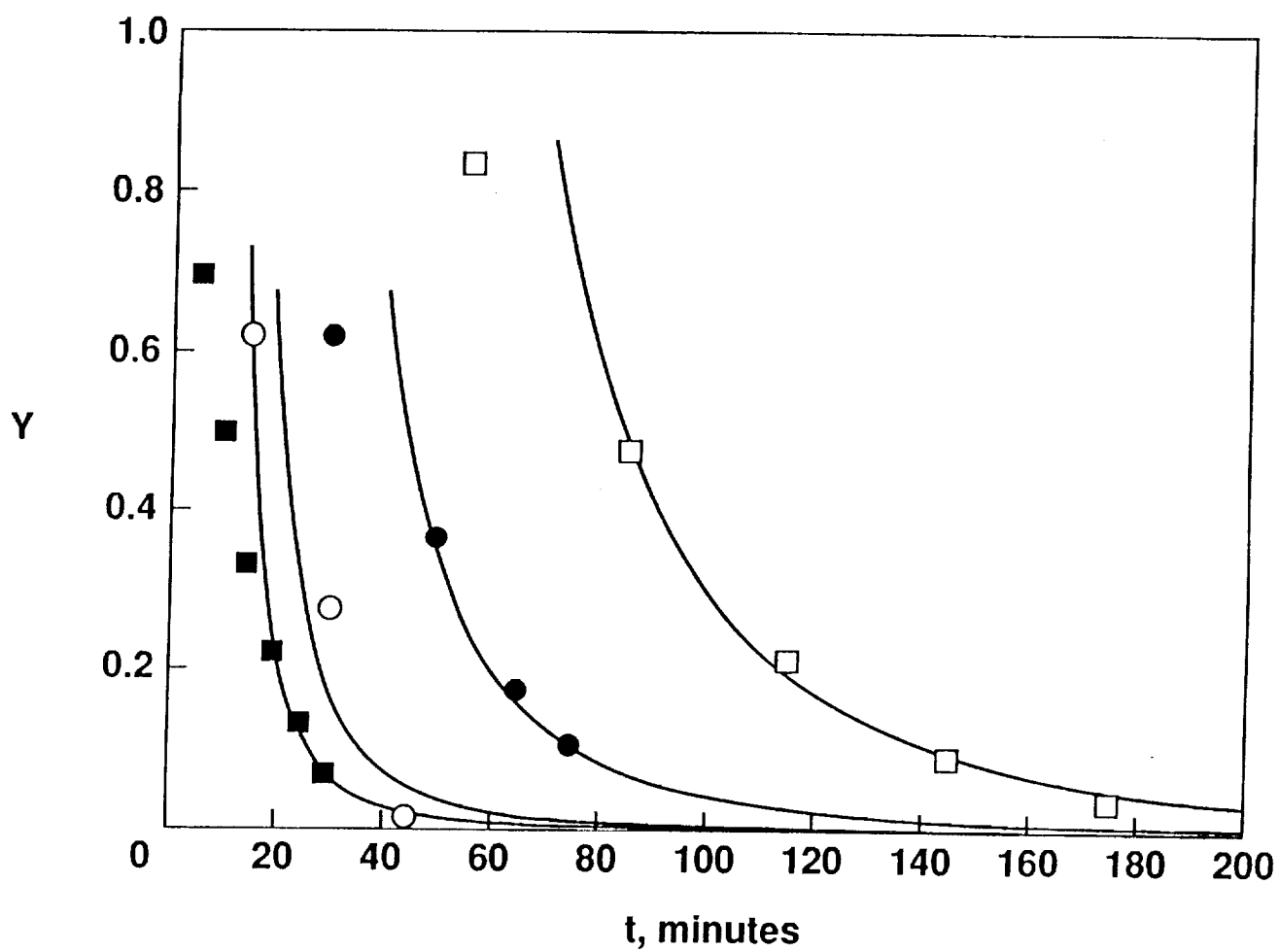


Figure 16. Recrystallization kinetics of the MTC-LV polymer. Symbols represent measurement values. Solid curves are Eq. (4) with parameters values tabulated in Table 4.

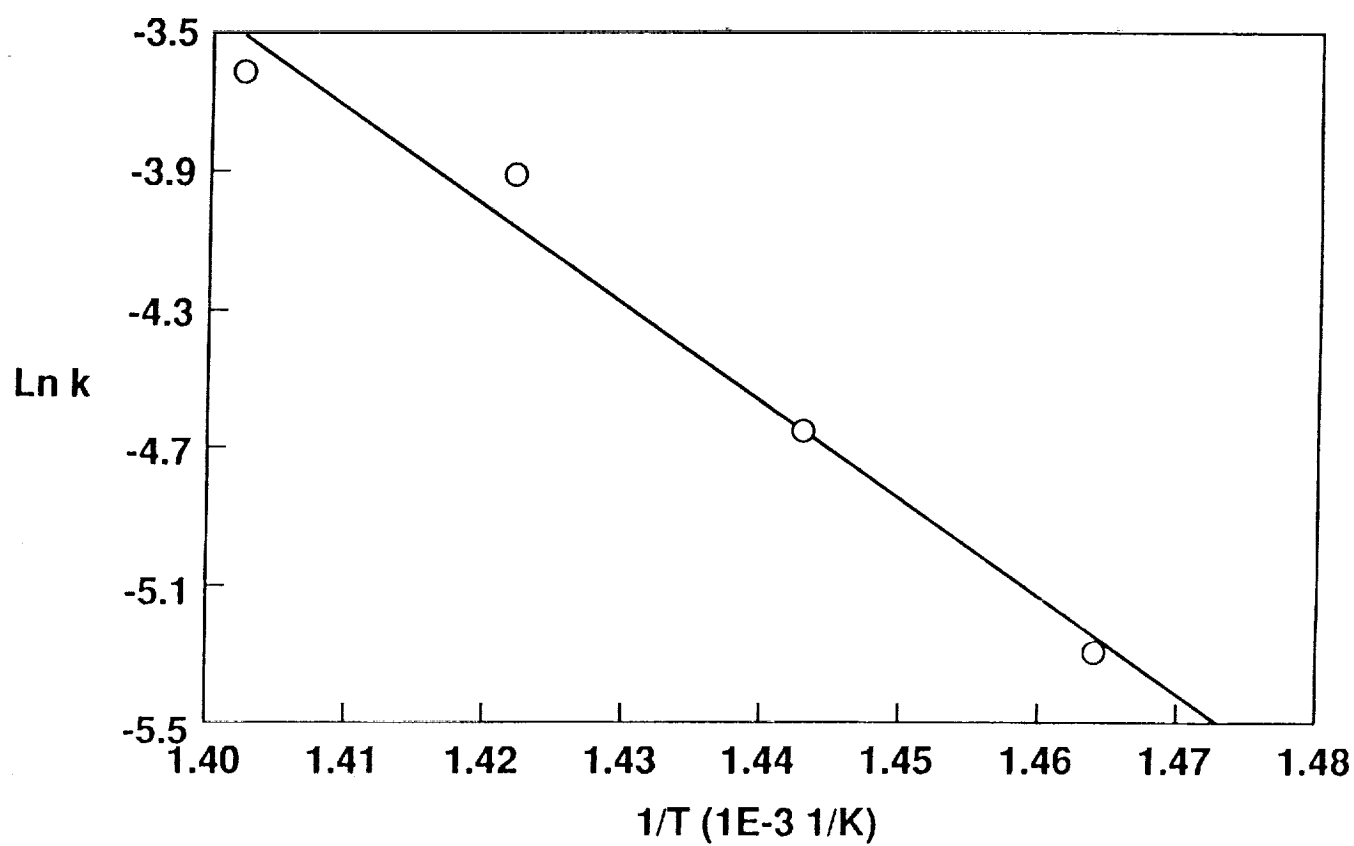


Figure 17. Arrhenius plot of Eq. (3) compared with the measurements.

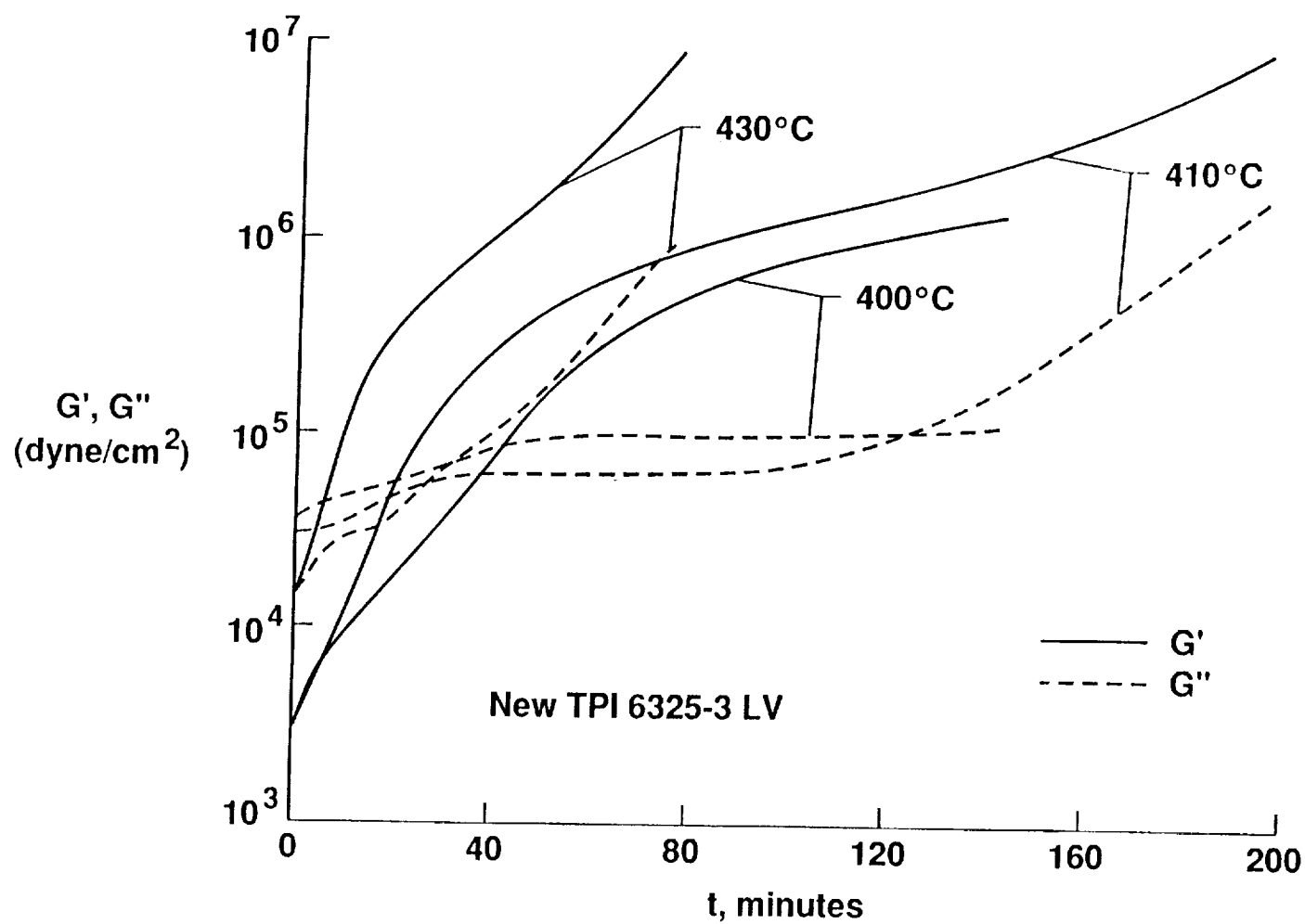


Figure 18. Storage and Loss moduli of the MTC-LV samples subjected to isothermal annealing at the temperatures indicated.



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16. Abstract Thermal and rheological properties of a commercial thermoplastic polyimide, NEW-TPI [®] , were characterized. The as-received material possesses initially a transient crystallite form with a bimodal distribution in peak melting temperatures. After the meltings of the initial crystallite structures, the sample can be recrystallized by various thermal treatments. A bi-modal or single modal melting peak distribution is formed for annealing temperatures below or above 360°C, respectively. The recrystallized crystallinities are all transient in nature. The polymers are unable to be recrystallized after being subjected to elevated temperature annealing above 450°C. The recrystallization mechanism was postulated, and a simple kinetics model was found to describe the behavior rather satisfactorily under the conditions of prolonged thermal annealing. Rheological measurements made in the linear viscoelastic range support the evidence observed in the thermal analysis. Furthermore, the measurements sustain the manufacturer's recommended processing window of 400-420°C for this material.					
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